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Global Distribution and Local Impacts of Inadvertently Generated Polychlorinated Biphenyls in Pigments

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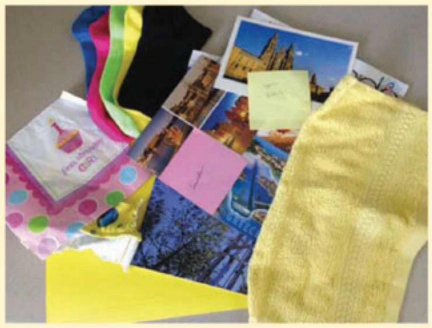
Supporting Information

ABSTRACT: The non-Aroclor congener 3,3′-dichlorobiphenyl (PCB 11) has been recently detected in air, water, sediment, and biota. It has been known since at least the 1970s that this congener is produced inadvertently during the production of certain organic pigments. PCB 11 was previously measured at parts-per-billion (ppb) levels in various printed materials obtained in the US. In this work, PCB 11 was detected in samples of common consumer goods including magazines, advertisements, maps, postcards, brochures, napkins, and garments from 26 countries in five continents at concentrations ranging from 0.27 to 86 ppb. Leaching tests confirmed that PCB 11 could be released from these materials into water. We also examined whether the known sources of PCB 11 were large enough to account for the levels of PCB 11 measured in the air, water, soil and sediment of the Delaware River Basin. A mass flow analysis suggests that the outflows and sequestration of PCB 11 in the basin total between 30 and 280 kg y^{-1}. If PCB 11 concentrations in pigments were at the maximum average (125 ppm) allowed under the Toxic Substances Control Act (TSCA), the estimated input of PCB 11 to the Delaware River Basin would be on the order of 42 kg y^{-1}. Despite the large uncertainty in these numbers, the results suggest that pigments may plausibly account for the levels of PCB 11 measured in the environment.



INTRODUCTION

Efforts in the United States to control polychlorinated biphenyl (PCB) contamination have generally focused on legacy PCB sources, such as Aroclors that were banned from production in the 1970s. PCBs are regulated as the sum of all 209 congeners, however, regardless of source. Recently, PCBs from non-Aroclor sources have received much attention. Among these non-Aroclor congeners is 3,3′-dichlorobiphenyl (PCB 11) that has been reported in various environmental media[1−6] thanks to US EPA's method development in congener-specific analysis of the entire PCB list.[7] PCB 11 was detected at levels often exceeding the federal water quality standard for the sum of PCBs (64 pg L^{-1}) in surface waters across the US.[8−13]

PCB 11 has mostly been associated with diarylide yellows, a group of dichlorobenzidine-based azo pigments that comprises the majority of classical organic yellow pigments,[8] but PCB 11 as well as other PCB congeners are found in a variety of pigments. The levels of PCB 11 that have been found in pigments vary widely. The Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry (ETAD) stated in 2011 that "...there are minute traces of inadvertently generated PCBs in some pigments (usually less than 5 ppm), and values up to 20 ppm have occasionally been measured···".[14] Some published reports indicated that levels of PCBs in pigments, inks, and paints were in the ppb range or lower,[8,14−19] but a few recent investigations reported detection up to 2,000 ppm of PCBs in some yellow pigments.[20−22] US and international law requires manufacturers of any product that may contain inadvertent PCBs to test their products. The maximum concentration of PCBs allowed in these products under the Toxic Substances Control Act (TSCA) in the US is an average of 25 ppm, not to exceed 50 ppm at any time.[23] However, the concentrations of mono- and dichlorobiphenyls are discounted in the calculation of the sum of PCBs. The present Code of Federal Regulations (40 CFR 761.3 from 2013) states the following: "For any purposes under this part, inadvertently generated non-Aroclor PCBs are defined as the total PCBs calculated following division of the quantity of monochlorinated biphenyls by 50 and dichlorinated biphenyls by 5".[23] In other words, pigments could contain an average of 125 ppm and a maximum of 250 ppm PCB 11 without exceeding the US federal limit. In the European Union, Council Directive 89/677/EEC set a limit of 50 ppm for the sum of PCBs in pigments with no discounting factors for mono- and dichlorobiphenyls.[24] These regulations cover not only the manufacture but also the processing and commercial distribution of PCB-containing products. Import is synonymous with manufacture under these regulations. Manufacturers are not required to disclose test results;, however, and in

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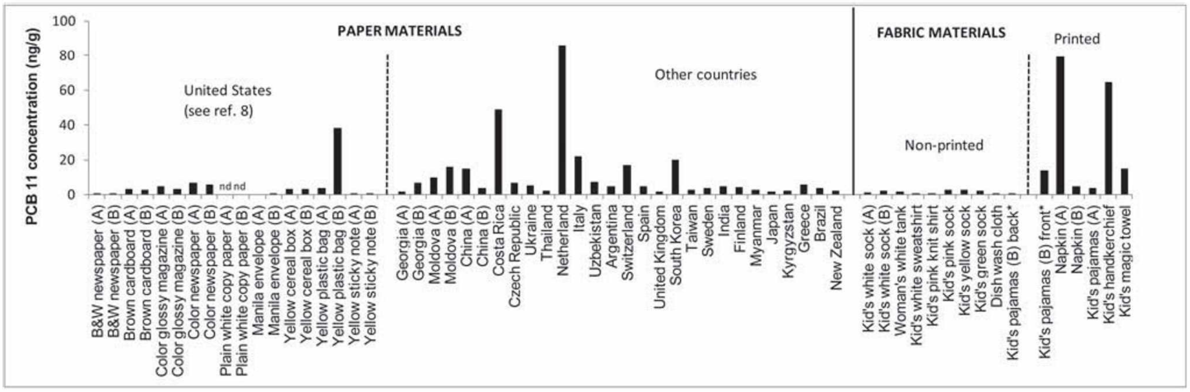

Figure 1. Concentrations of PCB 11 measured in printed materials (from the US previously reported[8]) and fabric materials. Only one sample of each material was analyzed. (A) and (B) represent the same type of materials but are not duplicates. Average concentrations reported where two extraction methods were used (see Table S1 of the Supporting Information). Clothing samples denoted with an asterisk (*) are the front and back pieces of the same garment. Note: nd = not detected, limit of detection = 0.10 ng g^{-1}.

many cases it is not clear whether testing is actually performed. In 2012, the Japanese ministries investigated byproduct PCBs in 588 organic pigments and found nearly 39% of tested items, mostly pigment reds and yellows, contained PCBs at concentrations from 0.5 to 2000 ppm.[20]

In response to the presence of PCBs in pigments used in printing inks in consumer goods, the State of Washington, USA, recently passed Bill 6086,[25] which states the following: "No [state] agency may knowingly purchase products or products in packaging containing polychlorinated biphenyls above the practical quantification limit except when it is not cost-effective or technically feasible to do so". The practical quantification limit using a method such as 1668 would be on the order of 1 ppb, or 50,000 times lower than the 50 ppm allowed under the TSCA.

World-wide production of color organic pigments was estimated to be about 250,000 t (t) in 2006, with about 25%, or 62,500 t, being diarylide yellows.[26] In the past decade, much of this production has shifted from the US and Europe to China and India. Thus, enforcement of TSCA and the European regulations now relies primarily on the testing of imported pigments. However, products that incorporate pigment, from raw inks to finished goods such as textile-printed clothing, are not tested. Assuming the average concentration of PCB 11 in diarylide yellow pigments is the maximum of 125 ppm, the maximum amount of PCB 11 produced by this route was about 7,800 kg y^{-1} worldwide as of 2006. The amount produced could be much smaller than this if the actual concentrations of PCBs in pigments are lower, but it could also be higher if pigments are not being tested for PCB levels and are routinely exceeding the levels set forth by TSCA, the Stockholm Convention, and the European Union's directives.

What fraction of the PCBs generated during pigment production is released to the environment? Is the amount of PCB 11 released to the environment from pigment use large enough to account for the levels of PCB 11 measured in environmental compartments? To answer these questions, we have constructed a mass flow analysis for the Delaware River. Like many urban waterways in the US, the Delaware River has been found to contain PCB 11 contamination even though no diarylide yellow pigment manufacturers were reported in this area (i.e., no facilities in the Toxics Release Inventory (TRI) report releases of 3,3′-dichlorobenzidine or related compounds used in pigment synthesis).[27] Therefore, the objectives of this study are (1) to establish that pigment applications dominated by printing inks is a source of PCB 11 worldwide; (2) to demonstrate that PCB 11 leaches out of printed materials into the water column; and (3) to assess the magnitude of emissions required to reach PCB 11 levels measured in the watershed and airshed of the Delaware River Basin and determine whether the known sources are adequate to produce the measured concentrations.

■ MATERIALS AND METHODS

Measurement of PCB 11 in Consumer Goods. Methods of measurement of PCB 11 and other congeners in printed materials such as newspapers and plastic bags were described previously.[8] Further details are provided in the Supporting Information. Because pigments are supplied globally with primary use in printing inks, PCB 11 was measured in samples of printed materials and other consumer goods that were collected from 26 countries in North America, South America, Europe, Asia, and Oceania. Paper from magazines, advertisements, maps, postcards, brochures, and a variety of textile and clothing for kids and adults were analyzed. The printed materials were stored for 1 day up to several weeks until being processed. The clothing was purchased a few days before analysis and was not washed before extraction.

Leaching Test of PCB 11 in Printed Materials. A simple 48-h column leach test was performed using milli-Q water as the leachant to evaluate the leaching potential of PCB 11 from printed materials with pigment use. Test materials included color newspapers, commercial flyers, and food and beverage packaging boxes collected in the US. Details are provided in the Supporting Information.

Mass Flow Analysis of PCB 11 in the Delaware River Basin. Import of PCB 11 into the Delaware River Basin was estimated in order to determine whether it is adequate to account for the measured and estimated stocks and flows of PCB 11 within and exiting the basin. Underpinning our analysis of mass flows is the assumption that the watershed is either at steady state with respect to PCB 11 flows or that PCB 11 flows and concentrations are increasing over time. This assumption is explored in more detail below. This analysis is based primarily

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on PCB concentrations measured by the Delaware River Basin Commission (DRBC) in surface water (2002–2003), sewage treatment plant influents and effluents (2005–2009), and surficial sediment (2008–2010) as part of the effort to develop a Total Maximum Daily Load (TMDL) for PCBs in the tidal Delaware River.[28,29] These data sets were all therefore collected under a Quality Assurance Project Plan (QAPP) approved by the US EPA and using EPA method 1668A.[7] Atmospheric PCBs were measured by active[30] and passive[6,31] sampling (2005–2011) as part of the Delaware Atmospheric Deposition Network (DADN). Eight soil samples were collected on the campus of Rutgers University in 2012 for PCB analysis. Major and minor removal processes of PCB 11 in the basin were selected for mass outflow estimates to be compared with total input from pigments. The results were further validated by a comprehensive Level III fugacity model.

RESULTS AND DISCUSSION

PCB 11 in Printed Materials. PCB 11 concentrations in printed materials sampled in the US were previously reported from nondetect to 38 ng g^{-1} (Figure 1).[8] PCB 11 levels in these products are many orders of magnitude lower than the levels of ΣPCBs found in carbonless copy paper in 1972, when PCB concentrations were reported as high as 64.7 mg g^{-1}.[32] Recycled paper may contain PCBs from recovery of carbonless copy paper, although the concentration has decreased due to volume reduction. Recycled PCB-containing paper has historically been used for food packaging with a tolerance limit of 10 ppm unless an impermeable barrier is present between the packaging material and food product (21 CFR 109.30 from 2004).[33]

In the present study, PCB 11 was detected from 1.5 to 86 ng g^{-1} in printed materials that were collected from another 25 countries on five continents (Figure 1). These findings suggest that printed materials may be a source of PCB contamination worldwide. PCB 11 was below the limit of detection (LOD = 0.10 ng g^{-1}) in samples of white copy paper and one of the manila envelopes.[8] This suggests that the presence of PCB 11 in the printed materials is due to the ink, not passive absorption from the atmosphere. Hence PCB 11 is primarily associated with color, especially yellow, printing. PCB 11 was by far the dominant PCB congener detected in the paper samples. Some other PCB congeners in the tri- through hexa-chlorinated homologues were also detected. Several studies in the US, Japan, and China reported PCB 11 detection in azo-type paint pigments that cover a range of vivid colors such as reds, oranges, and yellows.[18,21,22] Therefore, we conclude that PCB 11 is ubiquitously present as a byproduct in commercial pigment applications, particularly in printed materials.

PCB 11 in Fabric Materials. PCBs were also measured in a variety of dyed and pigment-printed clothing including knit shirts, pajamas, handkerchiefs, and socks for both kids and adults. Although the clothing samples were obtained in the US, most were manufactured outside the US in countries such as China and Honduras. PCB 11 concentrations in color fabrics varied between 0.27 and 79 ng g^{-1} (Figure 1 and Table S1). Some other PCB congeners such as PCB 52 (2,2′,5,5′-tetrachlorobipheny) that may also form from azo pigments[18,21] were also detected. PCB 11 was not detected in 2 of 3 laboratory blanks of quartz fiber filters (LOD = 0.10 ng g^{-1}). However, the concentration of PCB 11 in white clothing was around 1–2 ng g^{-1}, with most other PCB congeners below detection limit. This indicates that the fabric material is not acquiring PCB 11 through passive uptake from the air, because this process would allow a wide variety of congeners to accumulate in the fabric. Instead, PCB 11 may be entering the cloth via cross-contamination, probably during the production or dyeing of the cloth or the sewing and processing of the garment. Concentrations of PCB 11 in many of the other dyed materials were similar to those in the white clothing, indicating that these materials, too, may acquire PCB 11 as a cross-contaminant. All of the items with levels of PCB 11 well above 2 ng g^{-1} contained a printed design that did not penetrate through the fabric, a process known as textile printing of which 80% in the US uses pigments.[34] This design could have contained diarylide yellow or other pigments containing PCB 11. In one case, the front and back pieces from the same pajama top were extracted separately. PCB 11 concentration in the front piece printed in yellow was about 20 times more than that in the back piece dyed in red. Thus, PCB 11 in clothing primarily results from pigment, not dye, use. This is expected since dichlorobendine-based azo dyes are no longer manufactured because of their potential to release toxic amines.[35] Nevertheless, the presence of PCB 11 in clothing suggests that a primary route of entry of PCB 11 into wastewater is the washing of clothing. Future studies should assess the extent to which PCB 11 leaches out of clothing under conditions that simulate clothes washing (i.e., elevated water temperatures, presence of detergent and/or bleach).

Leaching of PCB 11 from Printed Materials. PCB 11 leached out of the test materials in all 22 experiments over the 48-h test using Milli-Q water as leachant. The fraction of PCB 11 that leached from printed materials ranged from 6% in a color newspaper and a product packaging box to 81% in a beverage packaging box (Figure S1). The varying fractions from the same type of material are likely due to pigments of different properties such as color and composition. Leaching of PCBs from these materials is likely to be more extensive under real-world conditions, because natural waters contain surfactant-like substances (such as humic acids)[36] and because materials could be exposed to leachant for longer than 48 h.

Taken together, the presence of PCB 11 in printed and fabric materials poses potential human exposure through dermal absorption. The environmental release of PCB 11 from these materials contributes additional routes of exposure via inhalation and digestion. In a few recent investigations, researchers detected PCB 11 and its hydroxylated metabolites in human sera collected from both urban community and rural areas with no historical PCB sources.[37,38] Nevertheless, the risk associated with PCB 11 among the general population was not assessed due to lack of data on toxicity and exposure.

Mass Flows of PCB 11 in the Delaware River Basin. In this mass flow analysis, we have assumed that the system is at or near steady state with respect to PCB 11 concentrations. This is not the case for Aroclor PCB congeners. For them, the sediments act as an internal load to the system, because they accumulated a PCB burden when concentrations were higher before the PCB ban of the 1970s and are releasing some of this reservoir now that concentrations have declined. The DRBC estimated that the sediments of the Delaware River contributed about 40% of the PCB burden in the water column.[27] We find it unlikely that this is the case for PCB 11, however, for several reasons. First, the production and use of color organic pigments has been relatively steady over time,[26,39] as opposed to the drastic reduction in Aroclor emissions following implementation of the TSCA. Second, Hu et al.[40] measured the

sedimentary PCB 11 profile in the Great Lakes and found that it matched the history of pigment production in the US. Assuming this is also true in the Delaware River, there is no gradient that would drive PCB 11 out of the sediments and into the water column. Third, we attempted to measure PCBs in a sediment core collected in Woodbury Creek near Philadelphia.[41] Most PCB congeners that are associated with Aroclors were detectable and displayed maximum concentrations at about 1975, with a decrease of a factor of 5 since then. In contrast, PCB 11 was not detectable in any of the core slices (LOD = 100 pg g^{-1}). This suggests that historical PCB 11 concentrations in the sediments of the Delaware River are relatively low and have stayed low for at least 50 years. Our measurements are in agreement with those of the DRBC, who measured an average concentration of PCB 11 in surficial sediments of the Delaware of 110 pg g^{-1}, and a median concentration of 30 pg g^{-1}.[28] Fourth, PCB 11 is much less hydrophobic and has a higher vapor pressure than most of the Aroclor congeners, such that it is primarily removed from the system via volatilization, and the sediments cannot retain a large enough reservoir to account for all of this volatilization. The top 10 cm of sediment in the Delaware River (with an area of about 2000 km^2) contains a median PCB 11 concentration of about 30 pg g^{-1}, which means this reservoir holds only about 3 kg of PCB 11 (assuming a solids concentration of 500 g L^{-1} in surficial sediments). For these reasons, our assumption that PCB 11 is at or close to steady state in the Delaware River Basin is justified, and the sediments are not an important source of PCB 11.

Mass Inflow into the Basin. As noted above, the worldwide PCB 11 production from diarylide yellow pigments was estimated to be as much as 7,800 kg y^{-1} in 2006 based on the maximum allowable concentration of PCB 11 in pigments of 125 ppm under the TSCA. Because some researchers have measured concentrations of PCBs in pigments as high as 2000 ppm, it is possible that worldwide production of PCB 11 is even higher. In addition, PCB 11 is found in other types of pigments. Since the pigment market has been either flat or growing slowly over the last few decades,[26] this estimate probably remains valid for the period of examination. The US market consumed 20% of color organic pigments produced worldwide in 2010.[42] Assuming that regional pigment use is proportional to population (the Delaware River Basin comprises 2.7% of US population[43]), PCB 11 imported into the basin via use of pigments is estimated to be 42 kg y^{-1} (or 115,000 mg d^{-1}) in 2006 if pigments contain 125 ppm of PCB 11. In comparison, the TMDL for ΣPCBs in Zones 2 through 6 of the Delaware River totals only 2,256 mg d^{-1}.[28,29]

Mass Outflow/Storage. Processes discussed in detail here are storage in landfills and outflow via volatilization from the land or water surface to the atmosphere. Sequestration in soil is likely to be large but cannot be estimated directly; it is addressed in the fugacity model (see below). Three other processes were also quantified, but they remove or sequester less than 1 kg y^{-1} of PCB 11, and so are discussed in the Supporting Information: outflow via the Delaware River to the Atlantic Ocean (0.068 kg y^{-1}), storage in the surficial sediment of the Delaware River (0.077 kg y^{-1}), and storage in the sludge from municipal wastewater treatment (0.28 kg y^{-1}). Other processes can be assumed to be negligible (see Supporting Information).

Storage in Landfills. PCB 11 may be sequestered in landfills along with paper and other pigment-containing products that are not recycled. In a survey of azo-colorants in Denmark, the final disposal of azo pigments associated with printing inks was distributed among landfill (24%), soil (7%), and incineration (69%).[44] Assuming these ratios are the same for PCB 11 in the Delaware River Basin, maximum sequestration of PCB 11 in landfill is estimated around 10 kg y^{-1} based on the maximum inflow of 42 kg y^{-1}. However, municipal solid waste (MSW) handling is quite different in the US,[45] where from 2000 to 2011 about 54% of all municipal solid waste was landfilled, about 12% incinerated, and about 26% recovered for recycling (but about 65% of this material was not actually recycled). It is not clear whether these percentages apply to printed materials. Paper and paperboard comprise about 28% of MSW, but pigments may also be present in food waste (via food packaging), textiles, and plastics. For paper and paperboard, about 54% is recovered for recycling, but the recycling process involves deinking which may release PCBs in the ink to the environment or may sequester them in the deinking waste. Only about 17% of textiles are recycled and just 1.7% of plastics. Based on these statistics, we estimate that 50% of all of the PCB 11 present in consumer products is landfilled. If the input of PCB 11 into the watershed is 42 kg y^{-1}, then this would imply that 21 kg y^{-1} is landfilled. Note that this estimate is dependent on the amount estimated to be imported into the estuary. If the estimated import were to change, then the absolute amount sequestered in landfills would also change, although the fraction (50%) stays the same.

Volatilization to the Atmosphere. The average concentration of atmospheric PCB 11 in the Delaware River Basin was about 6 pg m^{-3} with a small relative standard deviation (RSD) of 29% via passive air sampling conducted during March to June 2008.[31] A 2005 passive sampling campaign measured PCB 11 from 4 to 44 pg m^{-3} in the same airshed.[6] PCB 11 concentrations were mostly well above 6 pg m^{-3} from long-term monitoring of atmospheric PCBs by high-volume air sampling in this area. Specifically, airborne PCB 11 averaged 14 pg m^{-3} at Camden, New Jersey, 22 pg m^{-3} at New Brunswick, New Jersey, and 20 pg m^{-3} at Lums Pond, Delaware.[46]

A simple box model was constructed to calculate the emission required to maintain the average PCB 11 concentration in the airshed of the basin. Since the basin area is about 13,500 square miles, or 35,000 km^2, the airshed is assumed as a box with a square bottom in the same width (W) and length (L) of 187,000 m. The multimedia urban model (MUM), developed by Diamond et al.,[47] divides the air compartment into lower air from 0 to 50 m that is in contact with impervious surfaces and upper air from 50 to 500 m that is above most building heights. Therefore, two model scenarios were considered with atmospheric mixing height (H) of 50 and 500 m, respectively. Because the variation in PCB 11 concentrations measured in the air at the earth's surface is low, it is reasonable to assume that the box is well mixed.

The steady-state mass (M, g) of PCB 11 in the air box is calculated by eq 1

$$M = C_a \cdot W \cdot L \cdot H \qquad (1)$$

where C_a is the average PCB 11 concentration in the atmosphere (g m^{-3}); W, L, and H is the width, length, and height (m) of the air box, respectively. Major removal processes of PCB 11 from the atmosphere include advection by wind and reaction with hydroxyl (OH) radicals. Atmospheric deposition is negligible for low molecular weight PCBs such as PCB 11.[30]

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Table 1. Emission Rates and Concentrations of PCB 11 in the Delaware River Basin Calculated by the Level III Fugacity Model under Various Environmental Scenarios (A–D)[a]

	emission rate to bulk compartment ($kg\ y^{-1}$)						concentrations of PCB 11 in bulk compartment							
							air ($pg\ m^{-3}$)		water ($pg\ L^{-1}$)		soil ($pg\ g^{-1}$)		sediment ($pg\ g^{-1}$)	
model scenario	air	water	soil	sediment	total emission ($kg\ y^{-1}$)	air depth (m)	cald	repd	cald	repd	cald	repd	cald	repd
A	3.1	2.9	2.0	0	8.0	50	6.0	6	15.2	15.6	3.1	30	45	30
B	45	2.0	31	0	78	500	6.0		15.0		36		44	
C	2.9	2.0	21	0	26	50	20	20	15.8		27		47	
D	254	2.5	2.0	0	259	500	20		15.6		5.3		46	

[a]Reported median concentrations of PCB 11 in each bulk compartment are included for comparison.

The advective loss is calculated as a flushing rate (k_w, s^{-1}) by eq 2

$$k_w = u/W \tag{2}$$

where u is the wind speed ($m\ s^{-1}$). The average wind speed in the watershed was around 4 $m\ s^{-1}$.[48] The removal rate by reaction with OH radicals (k_{OH}, s^{-1}) is calculated by eq 3

$$k_{OH} = k \cdot C_{OH} \tag{3}$$

where k is the OH reaction rate constant ($2.2 \times 10^{-12}\ cm^3\ s^{-1}$) obtained from that of a similar dichlorobiphenyl, i.e. PCB 4, and C_{OH} is the global average concentration of OH radicals (9.7×10^5 molecules cm^{-3}).[49]

Finally, the emission rate (I, $mg\ d^{-1}$) is calculated as the product of steady-state mass of PCB 11 in the air box and the sum of all rate constants using eq 4.

$$I = M \cdot (k_w + k_{OH}) \cdot 1000 \cdot 86400 \tag{4}$$

With an atmospheric mixing height of 50 m, an emission of 21,000 $mg\ d^{-1}$ or 7.8 $kg\ y^{-1}$ is required to meet the most conservative estimate of average atmospheric PCB 11 concentration of 6 $pg\ m^{-3}$ in the basin. This is within the maximum estimated inflow of 42 $kg\ y^{-1}$. With an atmospheric mixing height of 500 m, an emission of 210,000 $mg\ d^{-1}$ or 78 $kg\ y^{-1}$ is required to produce an average concentration of 6 $pg\ m^{-3}$, which exceeds the maximum estimate of 42 $kg\ y^{-1}$. To achieve an average concentration of 20 $pg\ m^{-3}$, which is observed from active air sampling at Lums Pond, Delaware, an input of 26 $kg\ y^{-1}$ is needed if the mixing height is 50 m, and 260 $kg\ y^{-1}$ if the mixing height is 500 m. Because a typical height of 1–2 km vertical mixing is observed during daytime driven by convection from heated land surface and a stable boundary layer of 50–200 m is formed during the night,[50] both model scenarios have their own merit in describing the actual environmental conditions. However, the uncertainty in the mixing height renders the uncertainty in the estimated emissions very high.

It should be noted that PCB 11 inflow from upwind is assumed to be negligible because the background concentration is considered low surrounding the Delaware River Basin. This assumption is based in part on the measurements of Basu et al.,[51] who observed that PCB 11 concentrations were a function of population and were higher by a factor of about 7 between Chicago and a remote site. These researchers measured geometric mean concentrations of 18 $pg\ m^{-3}$ in Chicago versus 2.5 $pg\ m^{-3}$ in Eagle Harbor, Michigan. If the concentration of PCB 11 in the air flowing into the Delaware River Basin is 2.5 $pg\ m^{-3}$, the estimated mass flows of PCB 11 volatilizing from the river basin would be reduced by 3 $kg\ y^{-1}$ at a mixing height of 50 m and by 30 $kg\ y^{-1}$ at a mixing height of 500 m. In other words, the estimated volatilization of PCB 11 would then decrease to about 5 to 230 $kg\ y^{-1}$. Note that these estimates of volatilization are all independent of the amount of PCB 11 imported into the estuary.

Validation by Level III Fugacity Model. A level III fugacity model was applied to validate the mass flow estimates in a multimedia environment. Four bulk compartments including air, water, soil, and sediment containing four subcompartments including air, water, solid, and biota were considered according to the approach described by Mackay and Paterson.[52] The relevant compartmental properties including subcompartment volume fraction, density, organic carbon (OC) fraction, volume, area and depth are provided in Table S2 of the Supporting Information. The model incorporated partitioning between 10 subcompartments, 4 compartmental degradation processes, 13 intercompartmental transfers, and 2 advective flows in air and water. Transport parameters between bulk compartments and rates of advection and degradation within each bulk compartment are summarized in Tables S3 and S4 of the Supporting Information. Equilibrium was assumed between subcompartments within each bulk compartment but not between bulk compartments. The model not only examined the major removals calculated previously but also took into account the other dominant loss processes that were difficult to estimate such as sequestration in soil and soil-air transfer.

The parameters used in the model calculation were either collected from the literature[52] or measured in our laboratory. The atmospheric concentration of PCB 11 was relatively consistent with an average between 6 and 20 $pg\ m^{-3}$. Median concentrations of PCB 11 in the Delaware River were 15.6 $pg\ L^{-1}$ in the water column and 30 $pg\ g^{-1}$ in the sediment. PCB 11 was detected in one out of eight soil samples in the Delaware River Basin at a concentration of 80 $pg\ g^{-1}$ (LOD = 30 $pg\ g^{-1}$; data not shown). Chemical-specific properties (Table S5 of the Supporting Information) were used to calculate fugacity capacities (Z values) for each subcompartment and summed up for each bulk compartment. Transfer coefficients (D values) were calculated for intercompartmental transfers as well as intracompartmental advection and reaction. Finally, the emission rates were estimated to generate steady-state model output including all fugacities and concentrations. Table 1 lists four model scenarios (A–D) with varying emission rates into each bulk compartment to achieve the range of observed concentrations. No direct emission into sediment was assumed. Diagrams of PCB 11 mass flows in and between four bulk compartments for each model scenario are shown in Figure S2 of the Supporting Information. It should be noted that the emission rates were the most poorly quantified variables in the model; however, they offered invaluable capability of predicting

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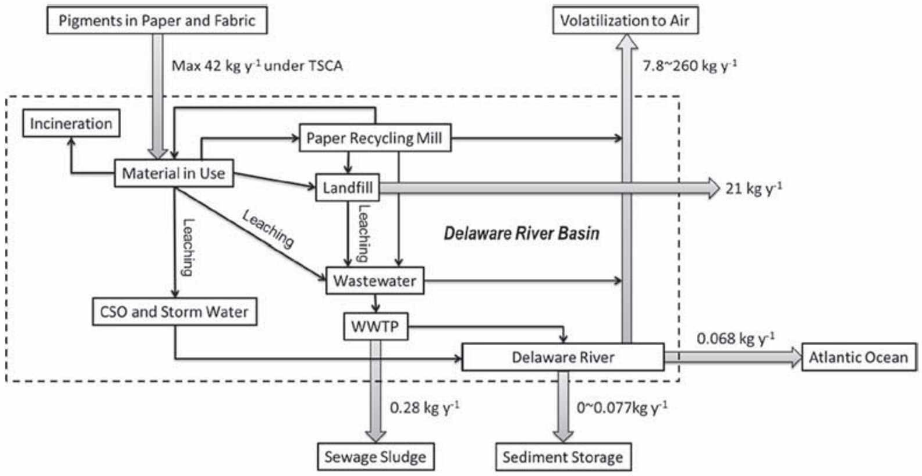

Figure 2. Mass flows of PCB 11 in the Delaware River Basin. External input from pigments is estimated using maximum average PCB 11 concentration (125 ppm) allowed under the TSCA. Estimated losses through volatilization, landfilling, advection, sedimentation, and sewage sludge removal are also given. Note: CSO stands for combined sewer overflows and WWTP stands for wastewater treatment plant.

the likely behavior of chemicals and estimating order of magnitude concentrations. By using the level III fugacity model, the estimated input of PCB 11 into the Delaware River Basin totaled from 8.0 to 259 kg yr^{-1}, which agrees well with previous calculations.

SUMMARY OF MASS FLOW ESTIMATES

Estimated mass flows of PCB 11 from production to distribution in the environment are summarized in Figure 2. Our study provides evidence that sources of PCB 11 are primarily associated with diarylide yellow and other pigments that are mostly applied in printing inks. The mass flow analysis of PCB 11 in the Delaware River Basin suggests that total inflows may be as high as 42 kg y^{-1} if pigments contain the maximum of 125 ppm of PCB 11 allowed under the TSCA. Total outflows range from about 30 to 280 kg y^{-1} by calculation of dominant loss processes and are supported by a level III fugacity model.

There are several implications to this mass flow analysis. First, it suggests that a substantial fraction of the PCB 11 contained within the products imported into the Delaware River Basin is released to the environment and can be measured in air, water, soil, and sediment. This is in stark contrast to the assertions of the ETAD, which has stated "...PCBs are present both on the surface and in the solid pigment matrix. This incorporated PCB is unlikely to lead either to human or environmental exposure. Additionally pigments are used to colour paints, inks and plastics and are themselves incorporated into a further matrix making release improbable−until both polymeric matrix and the pigments degrade."[14]

Second, the mass flow analysis suggests that pigments are a large enough source that they can plausibly account for the PCB 11 measured in the air, water, soil, and sediment of the Delaware River Basin. Other possible sources can be ruled out. Dichlorobenzidene-based dyes (as opposed to pigments) could theoretically be a source of PCB 11; however, 3,3′-dichlorobenzidine is no longer used to manufacture soluble dyes since 1986 in the US.[35] This compound is now mostly manufactured outside the US and imported for on-site processing or for use in pigment production.[35] Our investigation of PCB 11 levels in clothing suggests that they may come from pigments, rather than dyes. We know of no processes other than pigment use that could be responsible for the dispersion of PCB 11 in the environment. All of the source apportionment studies conducted for the New York/New Jersey Harbor and the Delaware River suggest that PCB 11 is not associated with Aroclors or microbial dechlorination but is instead correlated with stormwater and wastewater.[27,53] Furthermore, PCB 11 concentrations in the air and sediment of the Delaware River are evenly distributed throughout the watershed,[6,28,54] suggesting the sources are diffuse, as opposed to being associated with a small number of manufacturing facilities. Thus, whatever the source of PCB 11, it is related to some kind of human activity that is dispersed across the Delaware River Basin.

Finally, this investigation has demonstrated that the PCB 11 contained in consumer goods can leach into the environment, where humans and other biota can be exposed. We have demonstrated that this release is not only possible but appears to be extensive, such that most of the PCB 11 incorporated into consumer goods does escape the polymer matrix. Further research is needed to determine whether PCB 11 from pigments poses a risk to humans and biota.

ASSOCIATED CONTENT

Supporting Information

Additional information including 5 tables and 2 figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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Global distribution and local impacts of inadvertently generated polychlorinated biphenyls in pigments

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Supporting Information

5 tables

2 figures

Decline of Pigment Manufacture in the US

Chemicals listed in the US Toxics Release Inventory (TRI) that are associated with diarylide yellow pigment manufacture are 3,3'-dichlorobenzidine and 3,3'-dichlorobenzidine dihydrochloric acid. The total on- and off-site disposal and other releases of these chemicals have declined dramatically. In 1988, 14 facilities in the US released nearly 100,000 kg of these chemicals. By 2001, the number of facilities had declined to 4, generating 49,000 kg of total releases. In 2011, only one facility was still using these chemicals, generating 5 kg of waste. Despite this rapid decline in the US, worldwide pigment use was growing steadily during these years due to the shift of manufacturing base to Asia.

Analytical Methods of PCBs

Paper samples

Paper samples were analyzed in year 2009 and 2013. The samples from 2009 were processed as described previously.[1] In brief, each sample (~5 g) was spiked with PCBs 14, 23, 65, and 166 (Cambridge Isotope Laboratories, Andover, MA) as surrogates and extracted by Soxhlet in dichloromethane for 24 h. The maximum temperature achieved during Soxhlet extraction was the boiling point of dichloromethane, 40 °C. Since diarylide yellow is reported to be able to withstand temperatures of up to 180 to 200°C, breakdown of diarylide yellow to form PCB 11 during the extraction process is unlikely. The extracts were then reduced in volume by rotary evaporation and fractionated on a column of 3% water-deactivated alumina (60-325 mesh, Fisher Scientific, Pittsburgh, PA). The PCB fraction was eluted with hexane, concentrated under a gentle stream of nitrogen gas to about 0.5 mL, and injected with internal standards containing PCBs 30 and 204 (Cambridge Isotope Laboratories, Andover, MA).

Paper samples of 2013 were extracted in 3~5 g by an accelerated solvent extraction system (ASE 200, Dionex, Sunnyvale, CA). The ASE was operated at 100 °C and 1500 psi using either hexane/dichloromethane (3:1, v/v) or hexane as the extraction solvent. Deuterated PCBs 65 and 159 (C/D/N Isotopes, Inc., Quebec, Canada) were added as surrogates. The extracts were cleaned up by either 3% water-deactivated alumina as described above or 2.5% water-deactivated florisil (60-100 mesh, Fisher Scientific, Pittsburgh, PA). PCBs were eluted with hexane on the alumina column and petroleum ether on the florisil column. The PCB fraction was concentrated to 0.5 mL and spiked with deuterated PCBs 30 and 116 (C/D/N Isotopes, Inc., Quebec, Canada) as internal standards.

Clothing

Samples of clothing were extracted either in ~5 g using a Soxhlet or in 1~2 g using an ASE system as described above. The ASE was operated at 100 °C and 1500 psi using hexane/dichloromethane (3:1, v/v) as the extraction solvent. Deuterated PCBs 65 and 159 were added as surrogates. Soxhlet extracts were split into halves with one of them being processed for further analysis. Samples were cleaned up with either 3% water-deactivated alumina or 2.5% water-deactivated florisil as described above. All PCB fractions were concentrated to 0.5 mL and spiked with deuterated PCBs 30 and 116 as internal standards. Some clothing samples were analyzed with two methods (i.e. ASE extraction with alumina cleanup vs. Soxhlet extraction with florisil cleanup). The levels of PCB 11 measured in the same materials did not vary significantly between the two methods (Table S1), indicating that the elevated temperature and pressure in the ASE does not cause breakdown of the pigment or additional release of PCB 11,[2] and that both cleanup methods are acceptable for clothing samples. Measured concentrations varied within a factor of two for the same fabric processed by both ASE-alumina and Soxhlet-florisil methods. This variation may be due in part to the natural variation in concentration in different parts of the garment. This variation is expected to be particularly large in garments with a printed textile design.

Leaching tests

Two Teflon columns were prepared: one packed with ~15 g of shredded paper samples and the other filled with clean XAD-2 resin (Amberlite, Dow Chemical, Midland, MI). MilliQ water was pumped from a plastic reservoir first through the sample column and then the XAD-2 column at

a constant rate using a peristaltic pump (Masterflex L/S Easy Load II Pump, Cole-Parmer, Vernon Hills, IL). The test duration lasted approximately 48 hours. PCBs that leached from the sample column were sorbed by XAD-2 resin and thus leachate coming out of the XAD-2 column was free of PCBs. This was confirmed because no PCBs were detected in the leachate from the XAD-2 column; therefore, 2 L of MilliQ water was continuously pumped and reused throughout the test duration. Loaded XAD-2 resin was stored in acetone at 4 °C until extraction.

PCB analysis for XAD-2 resin resembled the procedure described previously.[3] Prior to extraction, all samples were injected with surrogates including either PCBs 14, 23, 65, and 166 or deuterated PCBs 65 and 159. Samples were Soxhlet extracted for 24 h in hexane/acetone (1:1, v/v) and then liquid-liquid extracted with 60 mL of Milli-Q water to separate the aqueous fraction from the organic fraction. The aqueous fraction was back-extracted three times with 50 mL of hexane and 1 g of NaCl in a separatory funnel. The extracts were then concentrated to ~ 1 mL and cleaned up on a 3% water-deactivated alumina column to collect the PCB fraction eluted with hexane. Finally the fraction was reduced in volume and injected with an internal standards containing either PCBs 30 and 204 or deuterated PCBs 30 and 116 for quantification.

GC/MS/MS analysis

Instrumental analysis of PCBs was performed by a gas chromatograph (6890N, Agilent, Santa Clara, CA) with a tandem quadrupole mass spectrometer (Quattro Micro GC, Waters, Milford, MA) by a modified EPA method 1668A as described previously.[4] It should be noted that either a DB-5 capillary column (60m×0.25mm× 0.25μm, Agilent Technologies, Santa Clara, CA) or an

SPB-Octyl capillary column (30m×0.25 mm×0.25μm, Sigma-Aldrich, St Louis, MO) was used for PCB analysis on the GC/MS/MS.

Temperature programs for both columns are specified as follows. For the DB-5 column, the initial oven temperature 70°C was increased at a rate of 7°C min^{-1} to 180°C, followed by 1.05°C min^{-1} to 225°C, then 5.75°C min^{-1} to 285°C, and 11.5°C min^{-1} to a final temperature of 300°C, holding for 20 min. For the SPB-Octyl column, the initial oven temperature was held at 75°C for 5 min, then increased at a rate of 15°C min^{-1} to 150°C, holding for 1 min, followed by 2.5°C min^{-1} to a final temperature of 280°C, holding for 3 min. The instrument was operated with an electron impact (EI) source under multiple reaction monitoring (MRM) mode. Ion transitions for each PCB homologue group are identical on both columns. PCB 11 was identified by monitoring the transition from precursor ion at m/z 222+224 to product ion at m/z 152 using authentic PCB 11 standard (Ultra Scientific, N. Kingstown, RI). The Frame solutions (Accustandard, Inc., New Haven, CT) containing all 209 PCB congeners were analyzed on both columns to confirm that no other di-CB congeners coeluted with PCB 11 in the chromatographic system. Internal standards PCB 30 or deuterated PCB 30 were used for quantification of PCB 11. Recoveries of surrogate standards PCB 23 or deuterated PCB 65 were reported for quality assurance.

Quality Assurance/Quality Control

Glass fiber filters (GFFs) or quartz fiber filters (QFFs) were analyzed as laboratory blanks for PCB 11 measurement in consumer goods. Pre-cleaned XAD-2 resin was used as the blank for leaching tests. GFFs and QFFs were baked at 450°C for 4 h prior to extraction. XAD-2 resins were Soxhlet extracted sequentially with methanol, acetone, hexane, acetone, and methanol for

24 h each and stored in MilliQ water before use. Teflon columns, tubings and cylinders were rinsed with methanol and MilliQ water prior to leaching tests. PCB 11 was below the detection limit in all laboratory blanks except three filter blanks. Recoveries of surrogate spiked onto paper samples ranged from 70% to 127 % for PCB 23 and from 49% to 78% for deuterated PCB 65. Surrogate recoveries of deuterated PCB 65 spiked onto clothing samples ranged from 22% to 122%. Recoveries of surrogate PCB 23 spiked onto selected XAD-2 resins ranged from 44% to 126%. Recoveries of the deuterated PCB 65 surrogate spiked onto XAD-2 resins ranged from 31% to 73%. PCB 11 concentrations were reported with correction by laboratory blanks and surrogate recoveries.

Mass Flow Analysis

Mass Flows Less Than 1 kg y^{-1}

Advection to the Atlantic Ocean

The median concentration of PCB 11 in Delaware River is about 15.6 pg L^{-1}. Based on 48 years of records collected by the USGS at Port Jervis, NY, the average flow of the Delaware River is 4,800 ft^3 s^{-1} or 1.2×10^{10} L d^{-1}.[5] Therefore, the mass flow of PCB 11 in the river under steady state is estimated to be 187 mg d^{-1} (0.068 kg y^{-1}).

Sedimentation via Particulate Matter

Sedimentation functions as a loss mechanism for PCB 11 in the Delaware River through burial into deeper layers of the sediment bed. In the Delaware River Total Maximum Daily Load (TMDL) model, two types of organic carbon were considered: biotic carbon (BIC) and particulate detrital carbon (PDC). Sedimentation of PCB 11 is expected to be primarily associated with PDC because its settling rate is much faster than that of BIC. The mass flow of

PCB 11 via settling of PDC into sediments (L_s, mg d^{-1}) is estimated by Eq. S1.

$$L_s = C_s \cdot A_s \cdot v_{PDC} \cdot C_{PDC,w}/1000 \qquad \text{(Eq. S1)}$$

where C_s is PCB 11 concentration in the sediments with a median of 30 pg g^{-1}; A_s is the water surface area around 2,000 km^2; v_{PDC} is the gross settling velocity of PDC that was assigned at 1 m d^{-1} in the water quality model developed by the Delaware River Basin Commission (DRBC);[6] and $C_{PDC,w}$ is PDC concentration in the water column ranging from 0 to 3.5 mg L^{-1}.[6] Therefore, the loss of PCB 11 via sedimentation was estimated to be from zero up to 210 mg d^{-1} or about 0.077 kg y^{-1}.

Removal via Sewage Sludge

The mass flow of PCB 11 sequestered in sewage sludge can be calculated from the removal efficiency of wastewater treatment plants (WWTPs). The input of PCB 11 into the WWTPs is roughly distributed between removal by sewer sludge and outflow with WWTP effluent. Removal efficiency of PCB 11 in WWTPs on the Delaware River is calculated to be between 63% to 94%.[7] We previously calculated that the load of PCB 11 from the top 12 discharger to the river totals about 190 mg d^{-1}.[1] Assuming an average removal efficiency of 80%, the mass flow of PCB 11 in sewage sludge is estimated as four times the effluent load of PCB 11 from the top 12 dischargers, or 760 mg d^{-1} (0.28 kg y^{-1}). Because the effluent load was calculated from geometric mean concentration and average daily flow rate, both measured by the dischargers, the uncertainty associated with this load estimate is relatively small and has been discussed earlier.[1]

Processes Assumed to Be Negligible

Reductive dechlorination of higher molecular weight PCBs (PCBs 77, 118, 126, 156 and 169)

could lead to elevated concentration of PCB 11 under anaerobic conditions in sediments.[8-11] However, none of these potential precursors to PCB 11 are primary constituents in any Aroclor mixtures or in the environment. In addition, our previous study examined the concentration ratios of PCB 11 to PCB 4, a characteristic dechlorination end product, in the Delaware River and concluded that the source of PCB 11 is different from that of PCB 4.[1] Furthermore, we examined the congener patterns of PCBs that are formed from dechlorination in this watershed and found that PCB 11 was not a significant product.[12] Therefore, it is unlikely that reductive dechlorination of heavier PCBs is responsible for the prevalence of PCB 11 found in the environment.

PCB 11 may be susceptible to aerobic degradation. Although some recent studies have isolated certain bacterial strains capable of growing on dichlorobiphenyls including PCB 11,[13] most microorganisms characterized in aerobic degradation of PCBs are mostly associated with monochlorobiphenyls and their growth frequently requires support from additional carbon sources such as biphenyl. There is no convincing data that demonstrate substantial degradation of PCB 11 in the environment. If such degradation did occur, it would only widen the discrepancy between the calculated inflow and outflow/storage of PCB 11 in the Delaware River Basin.

Table S1. PCB 11 concentrations in fabric materials measured by different extraction-cleanup methods (ND = not detected, Limit of Detection (LOD) = 0.10 ng g^{-1}).

Fabric Sample	Material	Color	Type of Coloring	PCB 11 (ng g^{-1})		
				ASE-Alumina	Soxhlet -Florisil	ASE-Florisil
Lab blank (GFF)	glass fiber filter	white		ND		
Lab blank (QFF)	quartz fiber filter	white			ND	
Kid's white sock (A)	cotton/polyester/ spandex	white	dyed			1.1
Kid's white sock (B)	cotton/polyester/ spandex	white	dyed			2.2
Woman's white tank	cotton/ polyester	white	dyed	1.6		
Kid's white sweatshirt	cotton/ polyester	white	dyed	0.41		
Kid's pink knit shirt	cotton/ polyester	dark pink	dyed	1.0	0.45	
Kid's pink sock	acrylic/polyester/ spandex	dark pink	dyed	3.0	2.2	
Kid's yellow sock	acrylic/polyester/ spandex	yellow	dyed	1.7	3.1	
Kid's green sock	acrylic/polyester/ spandex	green	dyed	1.9		
Dish wash cloth	cotton	light yellow	dyed	0.27		
Baby's luncheon napkins (A)	cellulose	yellow/red	printed	79		
Baby's luncheon napkins (B)	cellulose	pink/white	printed	4.6		
Kid's pajamas (A)	polyester	yellow	printed	4.7	2.5	
Kid's pajamas (B) front	cotton	yellow	printed	14		
Kid's pajamas (B) back	cotton	red	dyed	0.62		
Kid's handkerchief	cotton	yellow	printed	57	72	
Kid's magic towel	cotton	yellow/ orange	printed	15		

Table S2. Properties of the bulk compartments and sub-compartments: volume fraction of sub-compartment, density, organic carbon (OC) fraction, volume, area and depth.

bulk compartment	sub-compartment volume fraction				bulk compartment density (kg/m^3)	fraction OC in solids	volume (m^3)	area (m^2)	depth (m)
	air	water	solids	biota					
AIR	1.0	0	2×10^{-11}	0	1.19		$1.8 \times 10^{12} \sim 1.8 \times 10^{13}$	3.5×10^{10}	50 ~ 500
WATER	0	1.0	5×10^{-6}	1×10^{-6}	1000	0.2	4.0×10^{10}	2.0×10^{9}	20
SOIL	0.2	0.3	0.5	0	1500	0.02	3.3×10^{9}	3.3×10^{10}	0.1
SEDIMENT	0	0.7	0.3	0	1420	0.04	2.0×10^{7}	2.0×10^{9}	0.01
sub-compartment density (kg/m^3)	1.19	1000	2400	1000					

Table S3. Transport parameters between bulk compartments (MTC = mass transfer coefficient).

transport parameter	value
AIR-WATER	
air-side MTC over water	3 m h^{-1}
water-side MTC	0.03 m h^{-1}
rain rate	$9.7 \times 10^{-5} \text{ m h}^{-1}$
scavenging ratio	200000
dry deposition velocity	10.8 m h^{-1}
AIR-SOIL	
air-side MTC over soil	1 m h^{-1}
diffusion path length in soil	0.05 m
molecular diffusivity in air	$0.04 \text{ m}^2 \text{ h}^{-1}$
molecular diffusivity in water	$4.0 \times 10^{-6} \text{ m}^2 \text{ h}^{-1}$
WATER-SOIL	
solids runoff rate from soil	$2.3 \times 10^{-8} \text{ m h}^{-1}$
water runoff rate from soil	$3.9 \times 10^{-5} \text{ m h}^{-1}$
WATER-SEDIMENT	
water-side MTC over sediment	0.01 m h^{-1}
diffusion path length in sediment	0.005 m
molecular diffusivity in water	$4.0 \times 10^{-6} \text{ m}^2 \text{ h}^{-1}$
sediment deposition rate	$4.6 \times 10^{-8} \text{ m h}^{-1}$

sediment resuspension rate	1.1×10^{-8} m h^{-1}

Table S4. Rates of advection and degradation in each bulk compartment.

bulk compartment	advection		degradation	
AIR	wind speed	4 m s^{-1}	rate constant	7.68×10^{-3} h^{-1}
	air transfer rate to stratosphere	0.01 m h^{-1}		
WATER	water flow rate	1.2×10^{10} L d^{-1}	rate constant	0
SOIL	leaching rate from soil to groundwater	3.9×10^{-5} m h^{-1}	rate constant	0
SEDIMENT	sediment burial rate	3.4×10^{-8} m h^{-1}	rate constant	0

Table S5. Physical-chemical properties of PCB 11 from US EPA's EPISuite.

property	value
molecular weight	223 g mol^{-1}
vapor pressure	0.0948 Pa
water solubility	1.046 g m^{-3}
octanol-water partition coefficient ($logK_{ow}$)	5.27

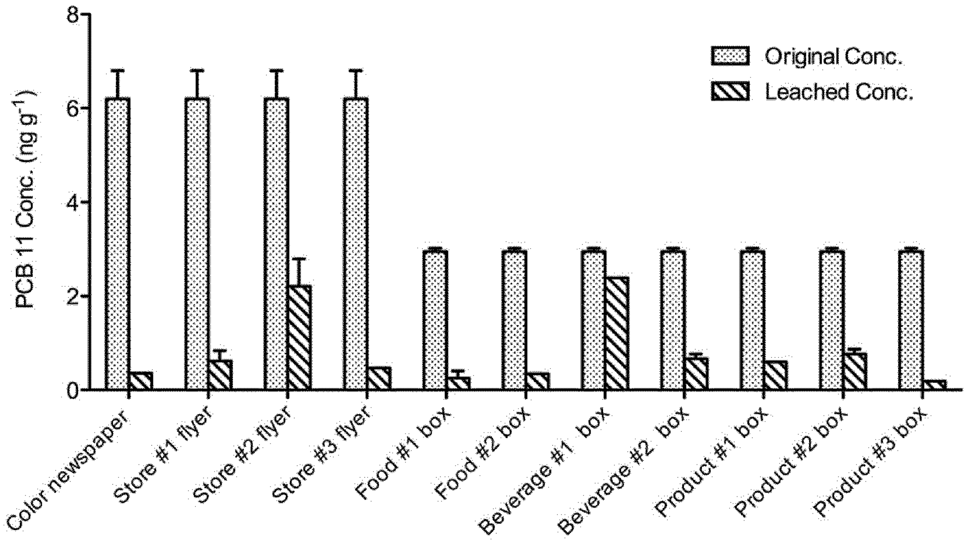
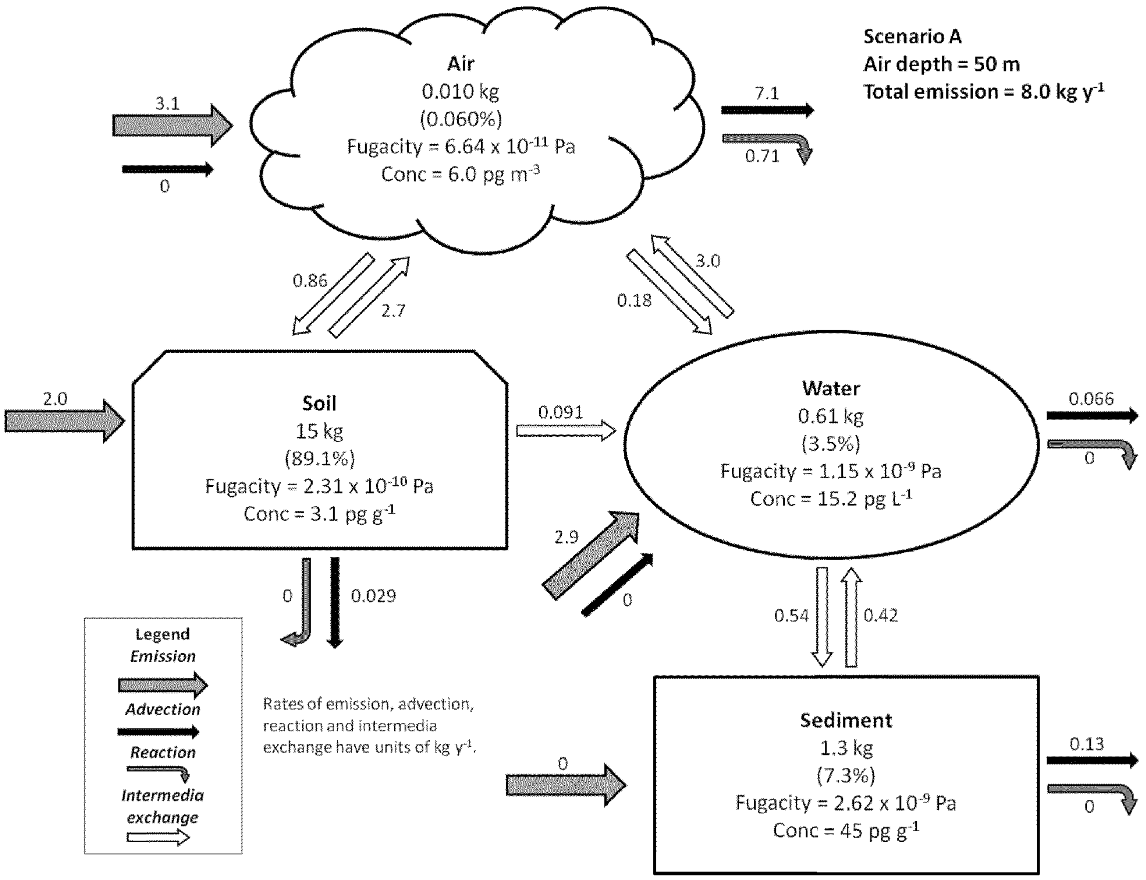
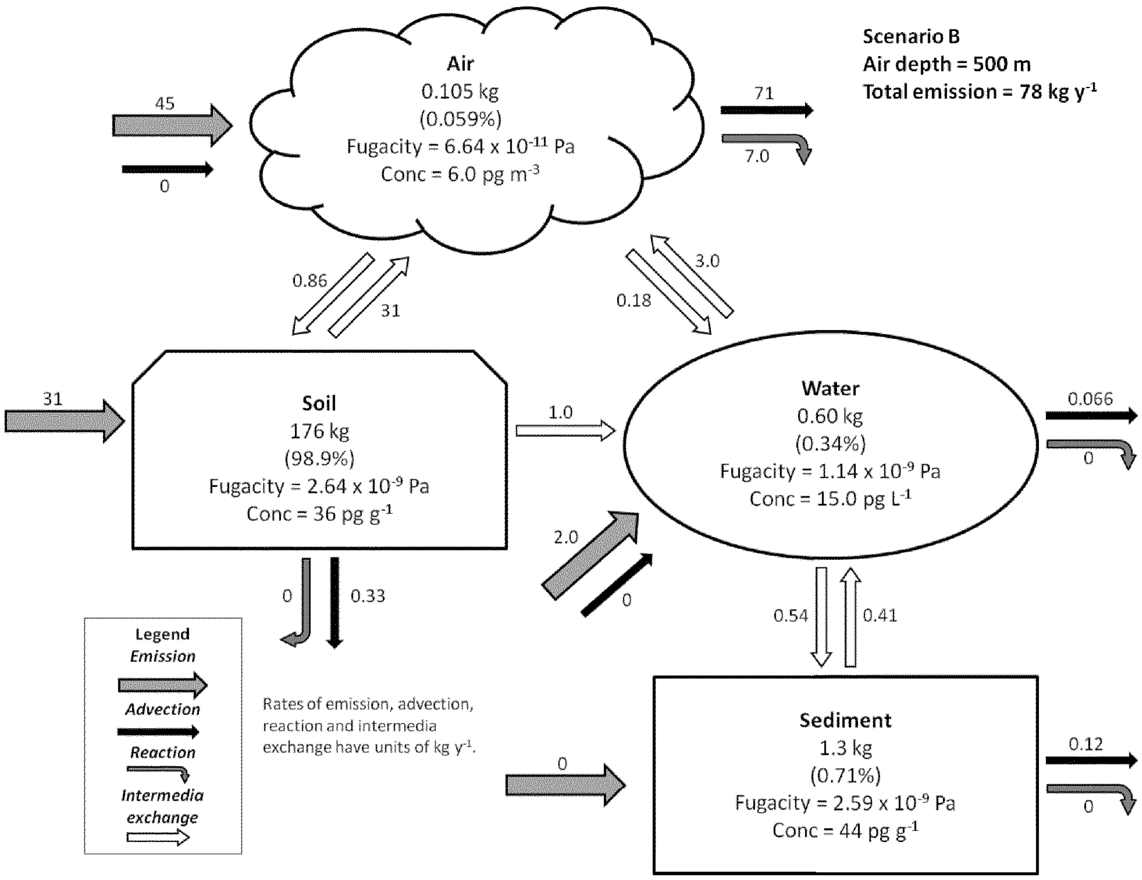
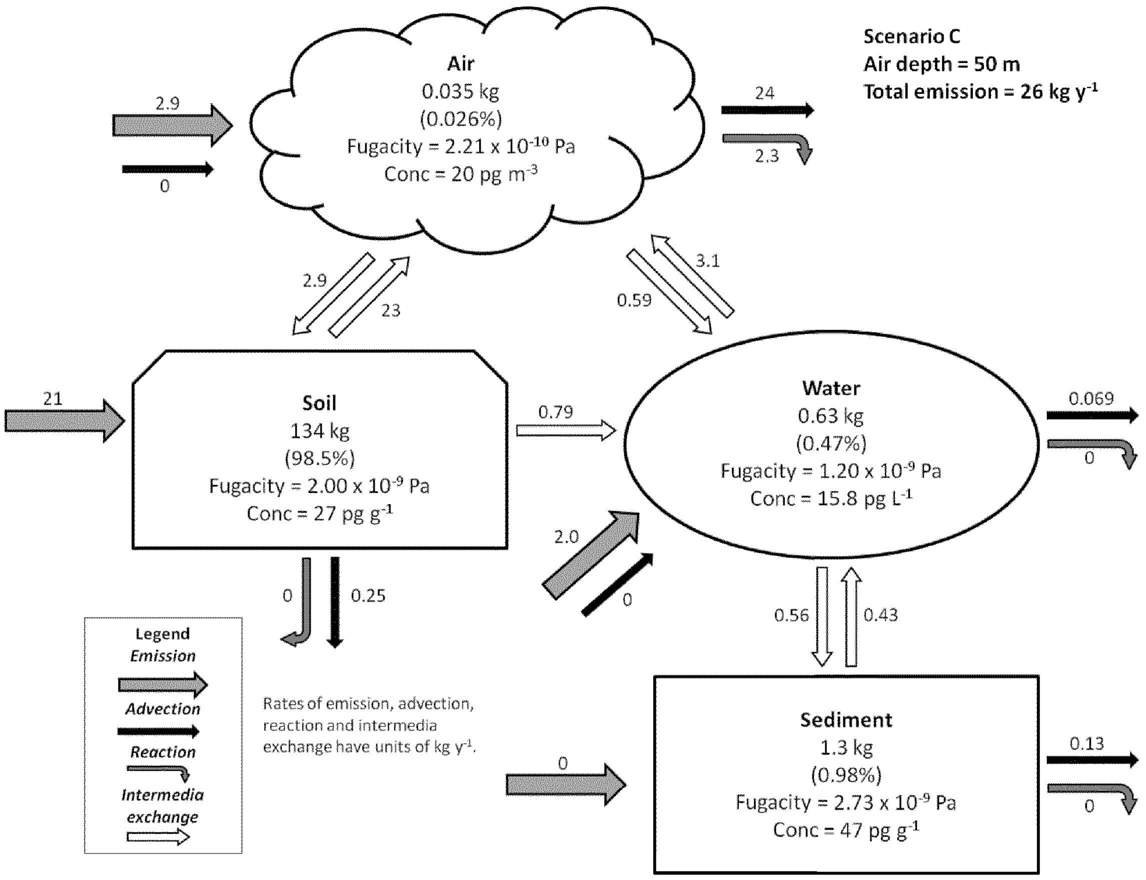


Figure S1. Original concentrations of PCB 11 (ng g^{-1}) in tested materials (dotted column) and leached concentrations of PCB 11 (ng g^{-1}) from respective materials (striped column). Error bar wherever displayed represents one standard deviation of measurements from multiple samples or leaching tests.



Scenario A
Air depth = 50 m
Total emission = 8.0 kg y-1
Air
0.010 kg
(0.060%)
Fugacity = 6.64 x 10-11 Pa
Conc = 6.0 pg m-3
3.1
0
7.1
0.71
0.86
2.7
3.0
0.18
2.0
Soil
15 kg
(89.1%)
Fugacity = 2.31 x 10-10 Pa
Conc = 3.1 pg g-1
0.091
Water
0.61 kg
(3.5%)
Fugacity = 1.15 x 10-9 Pa
Conc = 15.2 pg L-1
0.066
0
2.9
0
0
0.029
0.54
0.42
Legend
Emission
Advection
Reaction
Intermedia exchange
Rates of emission, advection, reaction and intermedia exchange have units of kg y-1.
0
Sediment
1.3 kg
(7.3%)
Fugacity = 2.62 x 10-9 Pa
Conc = 45 pg g-1
0.13
0


Scenario B
Air depth = 500 m
Total emission = 78 kg y-1
Air
0.105 kg
(0.059%)
Fugacity = 6.64 x 10-11 Pa
Conc = 6.0 pg m-3
45
0
71
7.0
0.86
31
3.0
0.18
Soil
176 kg
(98.9%)
Fugacity = 2.64 x 10-9 Pa
Conc = 36 pg g-1
31
1.0
Water
0.60 kg
(0.34%)
Fugacity = 1.14 x 10-9 Pa
Conc = 15.0 pg L-1
0.066
0
2.0
0
0
0.33
0.54
0.41
Legend
Emission
Advection
Reaction
Intermedia exchange
Rates of emission, advection, reaction and intermedia exchange have units of kg y-1.
0
Sediment
1.3 kg
(0.71%)
Fugacity = 2.59 x 10-9 Pa
Conc = 44 pg g-1
0.12
0


Scenario C
Air depth = 50 m
Total emission = 26 kg y-1
Air
0.035 kg
(0.026%)
Fugacity = 2.21 x 10-10 Pa
Conc = 20 pg m-3
2.9
0
24
2.3
2.9
23
3.1
0.59
Soil
134 kg
(98.5%)
Fugacity = 2.00 x 10-9 Pa
Conc = 27 pg g-1
21
0.79
Water
0.63 kg
(0.47%)
Fugacity = 1.20 x 10-9 Pa
Conc = 15.8 pg L-1
0.069
0
2.0
0
0
0.25
0.56
0.43
Legend
Emission
Advection
Reaction
Intermedia exchange
Rates of emission, advection, reaction and intermedia exchange have units of kg y-1.
0
Sediment
1.3 kg
(0.98%)
Fugacity = 2.73 x 10-9 Pa
Conc = 47 pg g-1
0.13
0

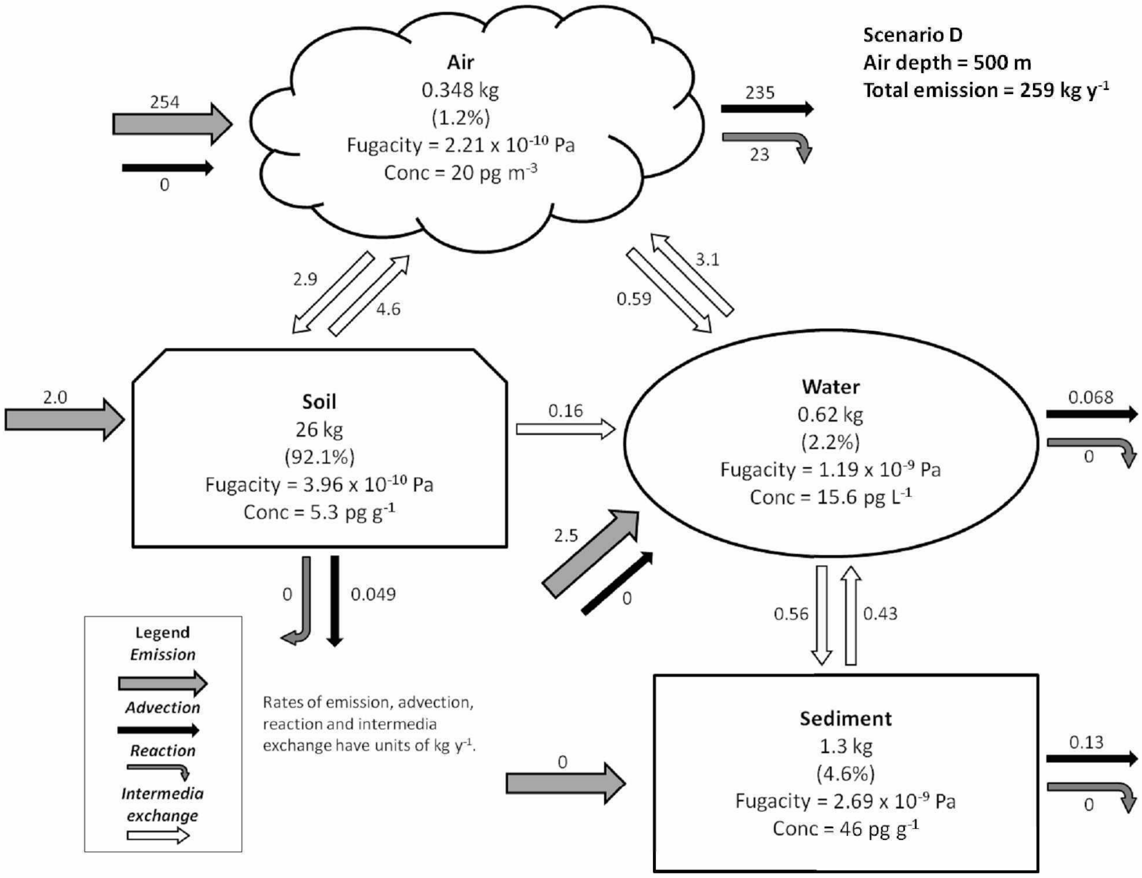


Figure S2. Distribution and mass flows of PCB 11 in the Delaware River Basin predicted by Level III fugacity model under various environmental scenarios (A-D).

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